ELECTRON BEAM CURING OF EPOXY ACRYLATE COATINGS ON MEDIUM-DENSITY FIBERBOARD

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ABSTRACT

Most of the medium-density fiberboard (MDF) as an engineered woods need surface coating process before entering final products, such as furniture and building materials. The wood surface should be covered for surface protection from damage during service life as well as to enhance its appearance. Surface coating of MDF was conducted using epoxy acrylate resin either for clear and pigmented coatings. Titanium dioxide was used for white pigmented coatings. Coating was conducted at variation thickness level of 30 to 150 µm. Curing was carried out by using 350 kV electron beam accelerator at 1.35 mA current and 1.6 m/min conveyor speed to get the absorbed dose of 3 Mrad. Effect of coating thickness was evaluated by measuring the physical, mechanical and chemical properties of cured samples, i.e., hardness, gloss, transparency, adhesion, abrasion resistance, and chemical, solvent and stain resistance. Experimental results showed that pendulum hardness and abrasion resistance slightly increased whereas gloss, transparency and adhesion resistance decreased with increasing coating thickness, while chemical, solvent and stain resistance remains similar. In general, clear coating provides better properties than pigmented coating.

***Keywords**: electron-beam; coating; epoxy-acrylate; pigment; medium-density fiberboard*

INTRODUCTION

The medium-density fiberboard (MDF) is a dry formed panel product manufactured from lignocellulosic fibers combined with a synthetic resin or other suitable binder. MDF has many advantages over plank wood, particle board, or high-density fiberboard, and appropriate for many applications. The surface is very smooth because the wood fibers used in its manufacture are uniform and fine. Coating of primer and top coat of paint take well, leaving an attractive finished surface unlike other composite wood products.

There are many application of MDF, such as for furniture, shelving, laminate flooring, decorative molding, and doors [1-3]. Most of the final products made of wood based materials need surface coating process in order to protect the material surface from defects caused by external effects (abrasion, scratch, chemicals, heat, weather, etc.) during service life and to enhance its performance by setting the color, texture and glossy.

In conventional process, curing of coating was conducted by addition of catalyst and can be speed up by heating. Besides of conventional process, surface coating can be performed by using electron beam (EB) as well as ultra violet (UV) radiation. EB-curable coatings contain no solvents and can be cured instantaneously (fast curing) without heat, and catalyst. A major advantage of EB-curing is that no volatile organic compound (VOC) or solvent emitted into the environment during the process and so the process is more friendly to the environment than conventional coating. Most of radiation curable systems contain acrylic monomers and acrylate-bearing oligomers due to the high curing speed [4,5]. Epoxy acrylate as one of the acrylate group has excellent properties, such as good chemical resistance, good adhesion to variety of substrates, excellent toughness, high hardness and better flexibility. The hydroxyl groups are formed by epoxy–acid reaction which markedly improve adhesion and pigment wetting [6]. Atta *et al.* [7], have developed new epoxy resins as organic coatings, based on the glycidyl ethers of the poly(ethylene terepthalate) waste with diethylene glycol and diethanol amine. This organic coatings can be used in lining for petroleum tanks and tankers, salt barges and ships, general chemical tankers, as well as exterior coatings for the bottoms, boot-topping, and decks.

Radiation curing using electron beam and ultra-violet have been developed for surface coating of several woods, such as tropical woods using clear coating [8,9]. EB-curing can also be used for prevention of the deterioration of marble using acrylic clear coating [10] and for reducing the processing time and cost while meeting the demanding requirement of high-performance composite structures [11]. Excellent physical, mechanical and chemical properties can be enhanced by the use of epoxy acrylate resin as radiation curable material.

The purpose of this study was to characterize the EB-curing of epoxy acrylate coatings on MDF either for transparent coating and pigmented coating using titanium dioxide as a white coloring. Effect of coating

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thickness on the physical, mechanical and chemical properties of EB-cured was the focus of this study.

EXPERIMENTAL SECTION

Materials

Medium-density fiberboard (250 mmx 12 mm X 4 mm) and aluminum plate (200 mm x 12 mm x 1mm) were used as the substrates for coating. Radiation curable material used was an epoxy acrylate resin with propietary name of Laromer EA 81 (the mixture of 80 % aromatic epoxy acrylate oligomer in hexandiol diacrylate monomer). The epoxy acrylate resin is highly viscous liquid and should be diluted with diluent to permit application. Difunctional monomer of tripropylene glycol diacrylate (TPGDA) was used to reduce the viscosity. Those chemicals are the products of BASF, Germany. Titanium dioxide pigment (TiO_2) with particle size of less than 1 µm (in polyester dispersion) was purchased from the local market, product of Matapel.

Equipments

Coating cn aluminum and MDF was performed by using glass rod after wounding with adhesive tape to get different thickness. An electron accelerator (350 keV, 10 mA) equipped with a conveyor system, at The Center for The Accelerator and Material Processing Technology, Yogyakarta, was used for irradiation of coated samples. Characterization of cured coating was conducted at The Center for The Application of Isotopes and Radiation Technology, Jakarta.

Experiments

Aluminum plate was cleaned with water followed by alcohol to get the surface free of dust, particles, fat, etc. MDF was sanded with # 240 abrasive papers to get smooth and even surface and followed by cleaning using alcohol. The radiation curable coatings were prepared by mixing the epoxy acrylate resin and TPGDA as a reactive diluent. In case of pigmented coating, the formulation was added with titanium dioxide as a pigment. The concentration of TPGDA and pigment were 10 wt% and 4 wt% respectively based on epoxy acrylate resin. Properties of MDF and coating formulations were tabulated in Table 1. The formulations with pigment (pigmented coating) and without pigment (clear coating) were coated on aluminum plate and MDF using glass rod after wounding with adhesive tapes to get the different coating thickness of 30, 60, 90, 120 and 150 µm. Coating on aluminum was carried out in order to measure the transparency and weight swelling ratio of cured coatings after releasing them from substrate. Coating on MDF was conducted in two steps, i.e, base coating and top coating. Base coating was conducted using clear coating at the thickness of around 30 µm, covered with 33 µm polyethylene film, and then exposed to EB radiation at the operating condition of 300 kV acceleration voltage, 1.35 mA current, and 1.6 m/min conveyor speed. The main purpose of the base coating is to fill any holes or cavities on the surface of wood panel. Top coating process was conducted by sanding the base coat with the same abrasive paper, coated with variation of thickness, covered with polyethylene film and irradiated at the same operating condition as did for base coating.

Measurement and testing

Coating thickness was measured using a Digimatic micrometer from Mitutoyo (Japan) with maximum deviation of 3 %. Weight swelling ratio and transparency of cured films were conducted after peeling off from aluminum substrate whereas for other measurements were conducted directly on the coated MDF. Weight swelling ratio was determined by immersing the samples in toluene at room temperature for 24 h. The sample surface was cleaned to remove the attached toluene, then immediately bottled and weighed. Weight swelling ratio (%) = $(W_s - W_o) \times 100 / W_o$, where W_s and W_o were weights after immersion and before immersion. Transparency of cured films was conducted using Spectrophotometer U-2000 of Hitachi (Japan), at the wave length of 369 nm for clear coating and 395 nm for pigmented coating. Pendulum hardness testing was conducted with a Koenig method using Pendulum hardness Rocker type from Sheen Instruments Ltd. (UK), according to ISO 1522-1973 (E). Adhesion between base coat and top coat in wood substrate was measured with a pull-off test method according ISO 4624-1978 using Elcometer model 106 Adhesion tester (UK). Adhesion test was also conducted using cross-cut method as described in ASTM D 2571-71.The specular gloss with 60° geometry was evaluated by means of glossmeter of Toyoseiki (Japan), according to ASTM D 523-85. Abrasion resistance was determined using a falling abrasion tester (natural silica sand) from specified height through a guide tube onto the coated wood, as described in ASTM D 968-81. The modification of abrasion resistance can be calculated from the equation, abrasion resistance = (D -L) x 100 % / D,

Table 1. Properties of MDF and radiation curable materials.

	Density (g/cm^3)	Moisture content (%)
MDF	0.72	9.2
	Density, 25 °C (g/cm^3)	Viscosity, 25 °C (cP)
Clear coating	1.10	2674
Pigmented coating	1.26	2750

where D and L are the diameter of inner tube (mm) and the length of shorter axis in the ellipse abraded area (mm), respectively. Chemical, solvent and stain resistance were performed with household chemicals using spot test method (ASTM D 1308).

RESULT AND DISCUSSION

Coating Formulations

Hexandiol diacrylate (HDDA) is a very low viscosity diluent which offers good cutting rate and high reactivity (M.W=226; Viscosity, 25 °C = 15 cps; % Shrinkage = 11.9%). Due to the straight line carbon backbone chain, HDDA offers the best combination of flexibility, adhesion, reactivity and toughness which is available in the difunctional acrylates. Identical with HDDA, TPGDA has a relatively low viscosity and good solvency for most acrylated polymers and offers high reactivity [12]. The dose required to reach the certain degree of curing decreases drastically with increasing functionality of the monomer. HDDA as a difunctional monomer give reliable curing by EB-radiation [13]. Kumar *et al.* [14], reported that incorporation of HDDA in the bisphenol diglycidyl ether diacrylate resin increasing degree of curing by electron beam radiation, supported by gel fraction and swelling studies.

Addition of TPGDA as amount as 10 wt% of resin decreases the viscosity from 3986 cp to 2674 cp, whereas addition of 4 wt% of pigment increasing the formulation from 2674 cp to 2750 and increasing the density 1.10 g/cm^3 to 1.26 g/cm^3. The viscosity of the coating formulations either for clear coating or pigmented coating formed even and smooth films appearance.

EB-Curing of Epoxy Acrylate Coatings

EB-curing relies on the penetration of electrons into a coating film, which is in turn, governed by their potential and the density of the coating. Absorption scatter and build-up occurring during the interaction between radiation and matter lead to dose gradients in the irradiated product, even if the absorbing materials is homogeneous. The range is approximately inverse proportional to the density of the absorbing material and approximately proportional to the energy of electron. For a given coating thickness, pigmentation in the formulation will considerably cut down the rate of cure [15].

The mechanism EB-curing trough radical polymerization covers initiation, propagation and termination step. In this system, the curing process occurred by means of copolymerization between epoxy acrylate oligomer either with HDDA and TPGDA monomers. The HDDA homopolymer and TPGDA homopolymer may be form in the system instead of copolymer, because TPGDA and HDDA are the multifunctional monomers with two double bonds that easily cross linked after exposed to EB-radiation. The surface cure will be inhibited in the presence of oxygen at the atmosphere above a coating during irradiation. Oxygen acts as the radical scavenger and will retard to the copolymerization reaction in acrylate system.

This is evident from the following reaction mechanism as the effect of oxygen [16].

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot} \quad (1)$$
$$R^{\cdot} + M \longrightarrow RM^{\cdot} \quad (2)$$
$$RO_2^{\cdot} + M \longrightarrow ROOM^{\cdot} \quad (3)$$

Oligomer radical ($R^{\cdot}$) reacts with oxygen produces peroxy radicals (reaction 1). The formation of peroxy radical competes with the formation of copolymer as a result of reaction between oligomer and monomer (M) (reaction 2). One of the peroxy radicals form, some parts of the monomer will also react with peroxy radicals to form another peroxy radicals ($ROOM^{\cdot}$). The reaction 3 proceeds so slowly that the chain reaction is virtually stopped. The effect of oxygen is especially pronounced at surfaces. It is not likely that oxygen molecules will penetrate much beyond the surface at the high intensity used. This can lead to a tacky or only partially cross link surface layer which may not have a good appearance and very low properties. Therefore, to minimize the oxygen concentration in the processing zone, several different techniques may be found for reducing or omitting oxygen concentration to a level at which the coating can be successfully cured. Inerting is needed and an inert gas as nitrogen is generally used. In this experiment, effect of oxygen from air is prevented by covering the coating using polyethylene film prior to irradiation.

Transparency

Most of the product made of MDF need pigmented coating to enhance their appearance and surface protection. The pigmented coating serves to hide the surface partly or completely depend on the degree of opacity requirement. In this case, the transparency measurement of film plays an important role to get the certain opacity. Its can be predicted that an increase film thickness would lead to decrease transparency, and transparency of clear film will be higher than pigmented film, as shown in Fig 1. Transparency of clear films are in the range of 50.7 % and 73 %, whereas for pigmented coating the transparency are in the range of 0 and 1.9 %. For coating thickness of 120 µm, surface of MDF was completely covered or hidden, as indicated by the transparency value of 0 %.

Weight swelling ratio

Weight swelling ratio (WSR) is a one measure to detect the cross link density of cured polymer. The higher the degree of cross-linking indicates the less free volume and segmental mobility remain available in

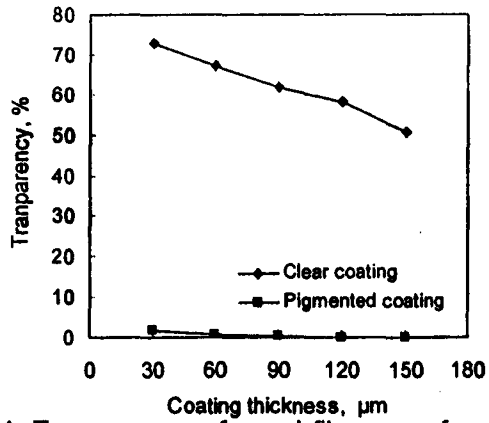

Fig 1. Transparency of cured films as a function of film thickness.

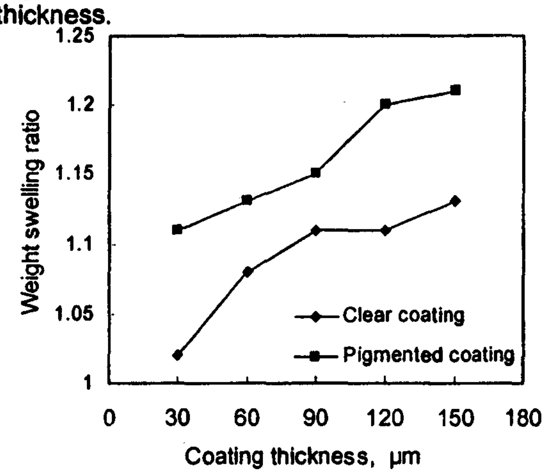

Fig 2. Weight swelling ratio cured films as a function of film thickness.

the polymer. So that solvent molecules can hardly penetrate the cross-link network at all. The higher the value of WSR, the lower the number of cross link polymer. WSR of cured polymer as a function of coating thickness is plotted in Fig 2. It is apparent from the figure that WSR increase with increasing coating thickness. There is a correlation between thickness and curing of coating. Increasing of film thickness, decreases of WSR. However, for the present of inorganic pigment (titanium dioxide) which has a density of about 4.9 g/cm^3, an electron beam of specified energy will not be able to penetrate to the depth it could in an unpigmented (clear) coating. In this respect, resin which has a density of 1.10 g/cm^3 increases to 1.26 g/cm^3 after addition of 4 wt % pigment. Absorption of radiation by thicker films and pigmented coating especially in the bottom of film influences the through cure in the free radical systems. Lowe [17], reported that addition of pigment in coating formulation can reduce the maximum attainable for curing of acrylate resin from 98-99 % to about 95 %. Increasing of thickness, decreasing of curing in the bottom of coating. In this site, the cross link polymer in pigmented coating was lower than that of clear coating.

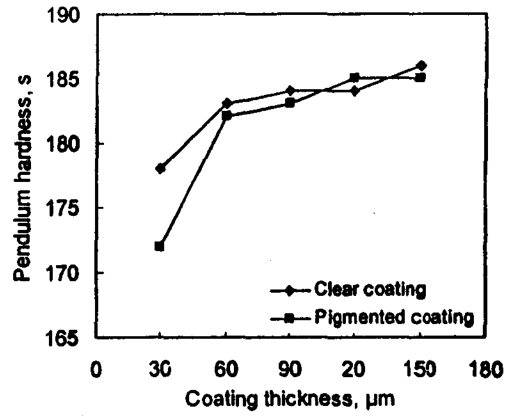

Fig 3. Pendulum hardness of cured coatings as a function of coating thickness.

The lower cross link polymer means the higher of swelling part, and finally increasing the value of WSR. The WSR of clear coatings were in the range of 1.02 - 1.12 whereas for pigmented coatings were in the range of 1.11 – 1.22.

Pendulum Hardness

Hardness is influenced by the thickness and the present of pigment in the coating. Fig 3 shows the plot of pendulum hardness of EB-cured coating on wood surface as a function of coating thickness. Pendulum hardness increased with coating thickness up to 60 μm and then remains unchanged. It can be observed, the optimum value were attained at the thickness of 60 μm. At this thickness level, the pendulum hardness were 182 s and 180 s for clear coating and pigmented coating respectively. The curves also indicate that the hardness of pigmented coatings were slightly lower than that of clear coatings for the same thickness. Lower coating thickness causes of lower values of the hardness. For low thickness (thin film), hardness of films may be affected by the substrate if the hardness of substrate is too low. It is possible that the substrate influences the measurement for low coating thickness. The pendulum hardness is not suitable for films with low thickness [18]. For very thick coatings on a matt substrate, such as MDF, the surface cure rate is independent of both the coating thickness and substrate reflectivity. As a note, the surface of MDF and base coat have pendulum hardness of around 46 s and 83 s, respectively. These values are much lower than that of coated MDF which the lowest hardness (172 s) was yielded by pigmented coating, whereas the highest value (187 s) was found for clear coating.

Abrasion resistance

Abrasion resistance increased with thickness up to 60 μm, and for higher thickness the abrasion resistance virtually unchanged (Figure 4). These results correlate

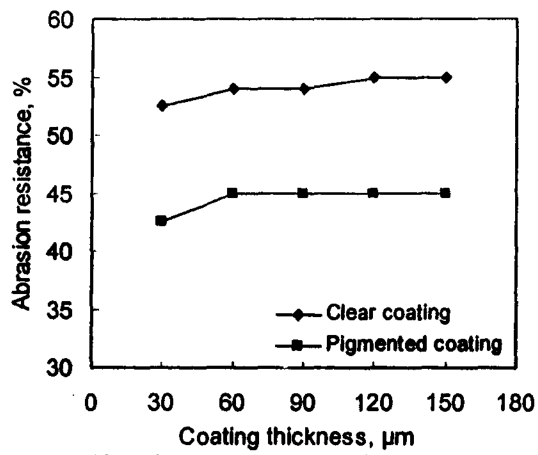

Fig 4. Abrasion resistance of cured coating as a function of coating thickness.

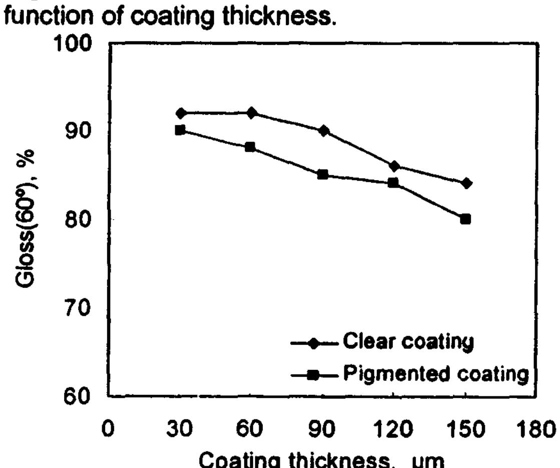

Fig 5. Gloss (60°) of cured coatings as a function of coating thickness.

well with the pendulum hardness test results. Abrasion resistance of clear coatings were higher than that of pigmented coating for the same thickness.

Generally, the abrasion resistance increased with increasing hardness and cross link density. The addition of pigment to the epoxy coating decreases abrasion resistance due to the less cross-link polymer occurred. The tend of abrasion resistance data was in line with the results of hardness (Fig 3). The more cross linked of cured coating, the better the abrasion resistance. Therefore, the increase in hardness, increases the resistant of coating to overcome the abrasion that tend to remove the film from wood substrate [19]. Abrasion resistance was in the range of 52.5 % - 56 % for clear coating whereas for pigmented coating were in the range of 45 % - 47.5 %.

Gloss

Gloss property usually correlates with the performance of coated products. High gloss is often a desirable aesthetic feature of radiation curable coatings. Fig 5 shows the gloss at 60^0 geometry incident light of

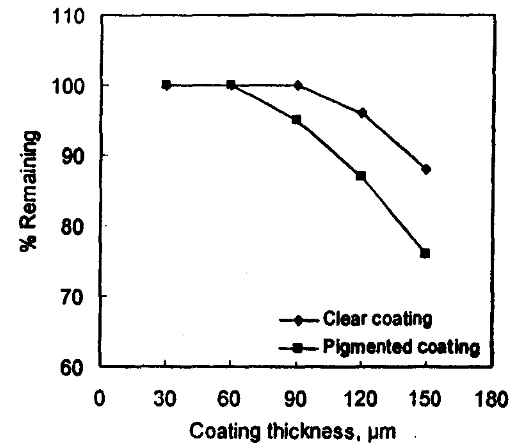

Fig 6. % Remaining of cured coatings as a function of coating thickness in adhesion measurement using cross-cut test.

cured coating as a function of coating thickness. In this case, there are three types of coating appearance i.e., clear, semi transparent and opaque coatings. Substrate and coating roughness, reflectance and transmittance of the coating influence the part of the light absorbed by the coating itself and another part by the substrate [20]. Specular gloss measurement is based on the part of the reflected light by the coating. The reflected light caused by the pigment in the coating is not measured at precisely the same angle as the incident light. The scattering of light reducing the sharpness of the gloss and appearance, but enhancing the haze of coatings. Maximum opacity and maximum gloss with a minimum haze can be achieved by the dispersion of pigment. In case of clear coating, even the substrate absorbs the light as indicated by the low gloss of wood substrate (1.5 %), but, reflection by coating is more dominance than that of scattering effect by pigment in pigmented coating. The higher thickness of pigmented coating enhances haze and reduces the specular gloss. As shown from the Fig 5, for same thickness clear coating provides slightly higher gloss than pigmented coating. The gloss of clear and pigmented coating were in the range of 75 % - 92 % and 74 % and 90 % respectively.

Adhesion

The adhesion strength on wood surface was measured by both cross-cut and pull-off test method. The qualitative adhesion of a coating to substrate can be tested by observing the amount of scored coating which is removed from the substrate by pressure sensitive adhesive. In cross-cut method, higher % remaining means higher adhesion. It can be observed from Fig 6 that percent remaining decreased with increasing thickness in the adhesion measurement using cross-cut test. It also clearly that adhesion of transparent coatings on wood substrate was better base coat. In general, clear coating provides better physical, mechanical and chemical properties than pigmented coating.

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